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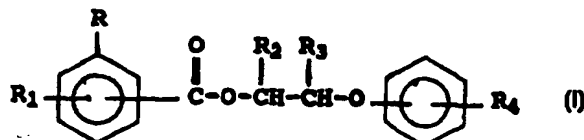
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(54) Title: FUEL ADDITIVE COMPOSITIONS CONTAINING AROMATIC ESTERS OF POLYALKYLPHENOXYALKANOLS AND POLY(OXYALKYLENE) AMINES



(57) Abstract

A fuel additive composition comprising: (a) an aromatic ester compound of formula (I), or a fuel soluble salt thereof, wherein R is hydroxy, nitro or  $-(CH_2)_n-NR_5R_6$ , wherein  $R_5$  and  $R_6$  are independently hydrogen or lower alkyl having 1 to 6 carbon atoms and X is O or I;  $R_1$  is hydrogen, hydroxy, nitro or  $-NR_7R_8$ , wherein  $R_7$  and  $R_8$  are independently hydrogen or lower alkyl having 1 to 6 carbon atoms;  $R_2$  and  $R_3$  are independently hydrogen or lower alkyl having 1 to 6 carbon atoms; and  $R_4$  is a polyalkyl group having an average molecular weight in the range of about 450 to 5,000; and (b) a poly(oxyalkylene) amine having at least one basic nitrogen atom and a sufficient number of oxyalkylene units to render the poly(oxyalkylene) amine soluble in hydrocarbons boiling in the gasoline or diesel fuel range. The fuel additive compositions of this invention are useful as fuel additives for the prevention and control of engine deposits.

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FUEL ADDITIVE COMPOSITIONS CONTAINING  
AROMATIC ESTERS OF POLYALKYLPHENOXYALKANOLS  
AND POLY(OXYALKYLENE) AMINES

BACKGROUND OF THE INVENTION

Field of the Invention

This invention relates to fuel additive compositions containing aromatic esters of polyalkylphenoxyalkanols and poly(oxyalkylene) amines. In a further aspect, this invention relates to the use of these additive compositions in fuel compositions to prevent and control engine deposits.

Description of the Related Art

It is well known that automobile engines tend to form deposits on the surface of engine components, such as carburetor ports, throttle bodies, fuel injectors, intake ports and intake valves, due to the oxidation and polymerization of hydrocarbon fuel. These deposits, even when present in relatively minor amounts, often cause noticeable driveability problems, such as stalling and poor acceleration. Moreover, engine deposits can significantly increase an automobile's fuel consumption and production of exhaust pollutants. Therefore, the development of effective fuel detergents or "deposit control" additives to prevent or control such deposits is of considerable importance and numerous such materials are known in the art.

For example, aliphatic hydrocarbon-substituted phenols are known to reduce engine deposits when used in fuel compositions. U.S. Patent No. 3,849,085, issued November 19, 1974 to Krauz et al., discloses a motor fuel

01 composition comprising a mixture of hydrocarbons in the  
02 gasoline boiling range containing about 0.01 to 0.25 volume  
03 percent of a high molecular weight aliphatic  
04 hydrocarbon-substituted phenol in which the aliphatic  
05 hydrocarbon radical has an average molecular weight in the  
06 range of about 500 to 3,500. This patent teaches that  
07 gasoline compositions containing minor amounts of an  
08 aliphatic hydrocarbon-substituted phenol not only prevent or  
09 inhibit the formation of intake valve and port deposits in a  
10 gasoline engine, but also enhance the performance of the  
11 fuel composition in engines designed to operate at higher  
12 operating temperatures with a minimum of decomposition and  
13 deposit formation in the manifold of the engine.

14  
15 Similarly, U.S. Patent No. 4,134,846, issued January 16,  
16 1979 to Machleder et al., discloses a fuel additive  
17 composition comprising a mixture of (1) the reaction product  
18 of an aliphatic hydrocarbon-substituted phenol,  
19 epichlorohydrin and a primary or secondary mono- or  
20 polyamine, and (2) a polyalkylene phenol. This patent  
21 teaches that such compositions show excellent carburetor,  
22 induction system and combustion chamber detergency and, in  
23 addition, provide effective rust inhibition when used in  
24 hydrocarbon fuels at low concentrations.

25  
26 Amino phenols are also known to function as  
27 detergents/dispersants, antioxidants and anti-corrosion  
28 agents when used in fuel compositions. U.S. Patent  
29 No. 4,320,021, issued March 16, 1982 to R. M. Lange, for  
30 example, discloses amino phenols having at least one  
31 substantially saturated hydrocarbon-based substituent of at  
32 least 30 carbon atoms. The amino phenols of this patent are  
33 taught to impart useful and desirable properties to  
34 oil-based lubricants and normally liquid fuels.

01 Similarly, U.S. Patent No. 3,149,933, issued September 22,  
02 1964 to K. Ley et al., discloses hydrocarbon-substituted  
03 amino phenols as stabilizers for liquid fuels.

04  
05 U.S. Patent No. 4,386,939, issued June 7, 1983 to  
06 R. M. Lange, discloses nitrogen-containing compositions  
07 prepared by reacting an amino phenol with at least one 3- or  
08 4-membered ring heterocyclic compound in which the hetero  
09 atom is a single oxygen, sulfur or nitrogen atom, such as  
10 ethylene oxide. The nitrogen-containing compositions of  
11 this patent are taught to be useful as additives for  
12 lubricants and fuels.

13  
14 Nitro phenols have also been employed as fuel additives.  
15 For example, U.S. Patent No. 4,347,148, issued August 31,  
16 1982 to K. E. Davis, discloses nitro phenols containing at  
17 least one aliphatic substituent having at least about  
18 40 carbon atoms. The nitro phenols of this patent are  
19 taught to be useful as detergents, dispersants, antioxidants  
20 and demulsifiers for lubricating oil and fuel compositions.

21  
22 Similarly, U.S. Patent No. 3,434,814, issued March 25, 1969  
23 to M. Dubeck et al., discloses a liquid hydrocarbon fuel  
24 composition containing a major quantity of a liquid  
25 hydrocarbon of the gasoline boiling range and a minor amount  
26 sufficient to reduce exhaust emissions and engine deposits  
27 of an aromatic nitro compound having an alkyl, aryl,  
28 aralkyl, alkanoyloxy, alkoxy, hydroxy or halogen  
29 substituent.

30  
31 More recently, certain poly(oxyalkylene) esters have been  
32 shown to reduce engine deposits when used in fuel  
33 compositions. U.S. Patent No. 5,211,721, issued May 18,  
34 1993 to R. L. Sung et al., for example, discloses an oil

01 soluble polyether additive comprising the reaction product  
02 of a polyether polyol with an acid represented by the  
03 formula  $\text{RCOOH}$  in which R is a hydrocarbyl radical having  
04 6 to 27 carbon atoms. The poly(oxyalkylene) ester compounds  
05 of this patent are taught to be useful for inhibiting  
06 carbonaceous deposit formation, motor fuel hazing, and as  
07 ORI inhibitors when employed as soluble additives in motor  
08 fuel compositions.

09  
10 Poly(oxyalkylene) esters of amino- and nitrobenzoic acids  
11 are also known in the art. For example, U.S. Patent  
12 No. 2,714,607, issued August 2, 1955 to M. Matter, discloses  
13 polyethoxy esters of aminobenzoic acids, nitrobenzoic acids  
14 and other isocyclic acids. These polyethoxy esters are  
15 taught to have excellent pharmacological properties and to  
16 be useful as anesthetics, spasmolytics, analeptics and  
17 bacteriostatics.

18  
19 Similarly, U.S. Patent No. 5,090,914, issued February 25,  
20 1992 to D. T. Reardan et al., discloses poly(oxyalkylene)  
21 aromatic compounds having an amino or hydrazinocarbonyl  
22 substituent on the aromatic moiety and an ester, amide,  
23 carbamate, urea or ether linking group between the aromatic  
24 moiety and the poly(oxyalkylene) moiety. These compounds  
25 are taught to be useful for modifying macromolecular species  
26 such as proteins and enzymes.

27  
28 U.S. Patent No. 4,328,322, issued September 22, 1980 to  
29 R. C. Baron, discloses amino- and nitrobenzoate esters of  
30 oligomeric polyols, such as poly(ethylene) glycol. These  
31 materials are used in the production of synthetic polymers  
32 by reaction with a polyisocyanate.

33  
34

01 U.S. Patent No. 4,859,210, issued August 22, 1989 to  
02 Franz et al., discloses fuel compositions containing (1) one  
03 or more polybutyl or polyisobutyl alcohols wherein the  
04 polybutyl or polyisobutyl group has a number average  
05 molecular weight of 324 to 3,000, or (2) a poly(alkoxylate)  
06 of the polybutyl or polyisobutyl alcohol, or (3) a  
07 carboxylate ester of the polybutyl or polyisobutyl alcohol.  
08 This patent further teaches that when the fuel composition  
09 contains an ester of a polybutyl or polyisobutyl alcohol,  
10 the ester-forming acid group may be derived from saturated  
11 or unsaturated, aliphatic or aromatic, acyclic or cyclic  
12 mono- or polycarboxylic acids.

13  
14 U.S. Patent Nos. 3,285,855, and 3,330,859 issued  
15 November 15, 1966 and July 11, 1967 respectively, to  
16 Dexter et al., disclose alkyl esters of dialkyl  
17 hydroxybenzoic and hydroxyphenylalkanoic acids wherein the  
18 ester moiety contains from 6 to 30 carbon atoms. These  
19 patents teach that such esters are useful for stabilizing  
20 polypropylene and other organic material normally subject to  
21 oxidative deterioration. Similar alkyl esters containing  
22 hindered dialkyl hydroxyphenyl groups are disclosed in U.S.  
23 Patent No. 5,196,565, which issued March 23, 1993 to Ross.

24  
25 U.S. Patent No. 5,196,142, issued March 23, 1993 to  
26 Mollet et al., discloses alkyl esters of hydroxyphenyl  
27 carboxylic acids wherein the ester moiety may contain up to  
28 23 carbon atoms. This patent teaches that such compounds  
29 are useful as antioxidants for stabilizing  
30 emulsion-polymerized polymers.

31  
32 Commonly assigned U.S. Patent No. 5,407,452, issued  
33 April 18, 1995, and corresponding International Application  
34 Publication No. WO 95/04118, published February 9, 1995,

01 disclose certain poly(oxyalkylene) nitro and aminoaromatic  
02 esters having from 5 to 100 oxyalkylene units and teach the  
03 use of such compounds as fuel additives for the prevention  
04 and control of engine deposits.

05  
06 Similarly, commonly assigned U.S. Patent No. 5,427,591,  
07 issued June 27, 1995, and corresponding International  
08 Application Publication No. WO 94/14926, published July 7,  
09 1994, disclose certain poly(oxyalkylene) hydroxyaromatic  
10 esters which are useful as fuel additives to control engine  
11 deposits.

12  
13 In addition, commonly assigned U.S. Patent No. 5,380,345,  
14 issued January 10, 1995, and corresponding International  
15 Application Publication No. WO 95/15366, published June 8,  
16 1995, disclose certain polyalkyl nitro and aminoaromatic  
17 esters useful as deposit control additives for fuels.  
18 Moreover, commonly assigned International Application  
19 Publication No. WO 95/11955, published May 4, 1995,  
20 discloses certain polyalkyl hydroxyaromatic esters which are  
21 also useful as deposit control fuel additives.

22  
23 Poly(oxyalkylene) amines are also well known in the art as  
24 fuel additives for the prevention and control of engine  
25 deposits. For example, U.S. Patent No. 4,191,537, issued  
26 March 4, 1980 to R. A. Lewis et al., discloses a fuel  
27 composition comprising a major portion of hydrocarbons  
28 boiling in the gasoline range and from 30 to 2000 ppm of a  
29 hydrocarbyl poly(oxyalkylene) aminocarbamate having a  
30 molecular weight from about 600 to 10,000, and at least one  
31 basic nitrogen atom. The hydrocarbyl poly(oxyalkylene)  
32 moiety is composed of oxyalkylene units selected from 2 to

33  
34



01 5 carbon oxyalkylene units. These fuel compositions are  
02 taught to maintain the cleanliness of intake systems without  
03 contributing to combustion chamber deposits.

04

05 U.S. Patent No. 5,112,364, issued May 12, 1992 to  
06 Rath et al., discloses gasoline-engine fuels which contain  
07 small amounts of a polyetheramine and/or a polyetheramine  
08 derivative, wherein the polyetheramine is prepared by  
09 reductive amination of a phenol-initiated or alkylphenol-  
10 initiated polyether alcohol with ammonia or a primary amine.

11

12 U.S. Patent No. 4,247,301, issued January 27, 1981 to  
13 Honnen, discloses hydrocarbyl-substituted poly(oxyalkylene)  
14 polyamines, wherein the hydrocarbyl group contains from 1 to  
15 30 carbon atoms and the polyamine moiety contains from 2 to  
16 12 amine nitrogen atoms and from 2 to 40 carbon atoms. This  
17 patent teaches that the additives may be prepared by the  
18 reaction of a suitable hydrocarbyl-terminated polyether  
19 alcohol with a halogenating agent, such as HCl or thionyl  
20 chloride, to form a polyether chloride, followed by reaction  
21 of the polyether chloride with a polyamine to form the  
22 desired poly(oxyalkylene) polyamine. This patent also  
23 teaches at Example 6 that the polyether chloride may be  
24 reacted with ammonia or dimethylamine to form the  
25 corresponding polyether amine or polyether dimethylamine.

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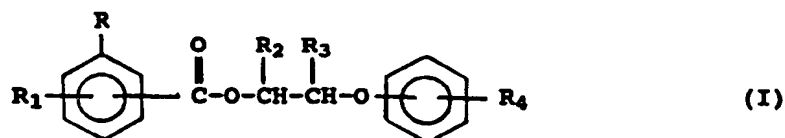
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SUMMARY OF THE INVENTION

It has now been discovered that the combination of certain aromatic esters of polyalkylphenoxyalkanols with poly(oxyalkylene) amines affords a unique fuel additive composition which provides excellent control of engine deposits, especially intake valve and combustion chamber deposits.

Accordingly, the present invention provides a novel fuel additive composition comprising:

- (a) an aromatic ester compound having the following formula or a fuel soluble salt thereof:



wherein R is hydroxy, nitro or  $-(CH_2)_x-NR_5R_6$ , wherein  $R_5$  and  $R_6$  are independently hydrogen or lower alkyl having 1 to 6 carbon atoms and x is 0 or 1;

$R_1$  is hydrogen, hydroxy, nitro or  $-NR_7R_8$ , wherein  $R_7$  and  $R_8$  are independently hydrogen or lower alkyl having 1 to 6 carbon atoms;

$R_2$  and  $R_3$  are independently hydrogen or lower alkyl having 1 to 6 carbon atoms; and

$R_4$  is a polyalkyl group having an average molecular weight in the range of about 450 to 5,000; and

01 (b) a poly(oxyalkylene) amine having at least one basic  
02 nitrogen atom and a sufficient number of oxyalkylene  
03 units to render the poly(oxyalkylene) amine soluble in  
04 hydrocarbons boiling in the gasoline or diesel fuel  
05 range.  
06

07 The present invention further provides a fuel composition  
08 comprising a major amount of hydrocarbons boiling in the  
09 gasoline or diesel range and an effective  
10 deposit-controlling amount of a compound of the present  
11 invention.  
12

13 The present invention additionally provides a fuel  
14 concentrate comprising an inert stable oleophilic organic  
15 solvent boiling in the range of from about 150°F. to 400°F.  
16 and from about 10 to 70 weight percent of a compound of the  
17 present invention.  
18

19 Among other factors, the present invention is based on the  
20 surprising discovery that the unique combination of certain  
21 aromatic esters of polyalkylphenoxyalkanols with  
22 poly(oxyalkylene) amines provides excellent control of  
23 engine deposits, especially on intake valves and in  
24 combustion chambers, when employed as additives in fuel  
25 compositions.  
26

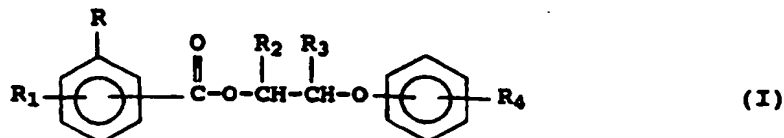
27 DETAILED DESCRIPTION OF THE INVENTION  
28

29 The Aromatic Ester of Polyalkylphenoxyalkanols  
30

31 The aromatic ester component of the present additive  
32 composition is an aromatic ester of a  
33  
34

-10-

01 polyalkylphenoxyalkanol and has the following general  
02 formula:



08 or a fuel-soluble salt thereof, wherein R, R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub>  
09 are as defined hereinabove.

10  
11 Based on performance (e.g. deposit control), handling  
12 properties and performance/cost effectiveness, the preferred  
13 aromatics ester compounds employed in the present invention  
14 are those wherein R is nitro, amino, N-alkylamino, or  
15 —CH<sub>2</sub>NH<sub>2</sub> (aminomethyl). More preferably, R is a nitro,  
16 amino or —CH<sub>2</sub>NH<sub>2</sub> group. Most preferably, R is an amino or  
17 —CH<sub>2</sub>NH<sub>2</sub> group, especially amino. Preferably, R<sub>1</sub> is  
18 hydrogen, hydroxy, nitro or amino. More preferably, R<sub>1</sub> is  
19 hydrogen or hydroxy. Most preferably, R<sub>1</sub> is hydrogen.  
20 Preferably, R<sub>4</sub> is a polyalkyl group having an average  
21 molecular weight in the range of about 500 to 3,000, more  
22 preferably about 700 to 3,000, and most preferably about 900  
23 to 2,500. Preferably, the compound has a combination  
24 of preferred substituents.

25  
26 Preferably, one of R<sub>2</sub> and R<sub>3</sub> is hydrogen or lower alkyl of 1  
27 to 4 carbon atoms, and the other is hydrogen. More  
28 preferably, one of R<sub>2</sub> and R<sub>3</sub> is hydrogen, methyl or ethyl,  
29 and the other is hydrogen. Most preferably, R<sub>2</sub> is hydrogen,  
30 methyl or ethyl, and R<sub>3</sub> is hydrogen.

31  
32 When R and/or R<sub>1</sub> is an N-alkylamino group, the alkyl group  
33 of the N-alkylamino moiety preferably contains 1 to 4 carbon  
34

01 atoms. More preferably, the *N*-alkylamino is *N*-methylamino  
02 or *N*-ethylamino.

03

04 Similarly, when *R* and/or *R*<sub>1</sub> is an *N,N*-dialkylamino group,  
05 each alkyl group of the *N,N*-dialkylamino moiety preferably  
06 contains 1 to 4 carbon atoms. More preferably, each alkyl  
07 group is either methyl or ethyl. For example, particularly  
08 preferred *N,N*-dialkylamino groups are *N,N*-dimethylamino,  
09 *N*-ethyl-*N*-methylamino and *N,N*-diethylamino groups.

10

11 A further preferred group of compounds are those wherein *R*  
12 is amino, nitro, or -CH<sub>2</sub>NH<sub>2</sub> and *R*<sub>1</sub> is hydrogen or hydroxy.

13 A particularly preferred group of compounds are those  
14 wherein *R* is amino, *R*<sub>1</sub>, *R*<sub>2</sub> and *R*<sub>3</sub> are hydrogen, and *R*<sub>4</sub> is a  
15 polyalkyl group derived from polyisobutene.

16

17 It is preferred that the *R* substituent is located at the  
18 meta or, more preferably, the para position of the benzoic  
19 acid moiety, i.e., para or meta relative to the carbonyloxy  
20 group. When *R*<sub>1</sub> is a substituent other than hydrogen, it is  
21 particularly preferred that this *R*<sub>1</sub> group be in a meta or  
22 para position relative to the carbonyloxy group and in an  
23 ortho position relative to the *R* substituent. Further, in  
24 general, when *R*<sub>1</sub> is other than hydrogen, it is preferred  
25 that one of *R* or *R*<sub>1</sub> is located para to the carbonyloxy group  
26 and the other is located meta to the carbonyloxy group.  
27 Similarly, it is preferred that the *R*<sub>4</sub> substituent on the  
28 other phenyl ring is located para or meta, more preferably  
29 para, relative to the ether linking group.

30

31 The compounds employed in the present invention will  
32 generally have a sufficient molecular weight so as to be  
33 non-volatile at normal engine intake valve operating  
34 temperatures (about 200°-250°C). Typically, the molecular

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01 weight of the compounds employed in this invention will  
02 range from about 700 to about 3,500, preferably from about  
03 700 to about 2,500.

04

05 Fuel-soluble salts of the compounds of formula I can be  
06 readily prepared for those compounds containing an amino or  
07 substituted amino group and such salts are contemplated to  
08 be useful for preventing or controlling engine deposits.  
09 Suitable salts include, for example, those obtained by  
10 protonating the amino moiety with a strong organic acid,  
11 such as an alkyl- or arylsulfonic acid. Preferred salts are  
12 derived from toluenesulfonic acid and methanesulfonic acid.

13

14 When the R or R<sub>1</sub> substituent is a hydroxy group, suitable  
15 salts can be obtained by deprotonation of the hydroxy group  
16 with a base. Such salts include salts of alkali metals,  
17 alkaline earth metals, ammonium and substituted ammonium  
18 salts. Preferred salts of hydroxy-substituted compounds  
19 include alkali metal, alkaline earth metal and substituted  
20 ammonium salts.

21

## 22 Definitions

23

24 As used herein, the following terms have the following  
25 meanings unless expressly stated to the contrary.

26

27 The term "amino" refers to the group: -NH<sub>2</sub>.

28

29 The term "N-alkylamino" refers to the group: -NHR<sub>a</sub> wherein  
30 R<sub>a</sub> is an alkyl group. The term "N,N-dialkylamino" refers to  
31 the group: -NR<sub>b</sub>R<sub>c</sub>, wherein R<sub>b</sub> and R<sub>c</sub> are alkyl groups.

32

33 The term "alkyl" refers to both straight- and branched-chain  
34 alkyl groups.

01 The term "lower alkyl" refers to alkyl groups having 1 to  
02 about 6 carbon atoms and includes primary, secondary and  
03 tertiary alkyl groups. Typical lower alkyl groups include,  
04 for example, methyl, ethyl, n-propyl, isopropyl, n-butyl,  
05 sec-butyl, t-butyl, n-pentyl, n-hexyl and the like.

06

07 The term "polyalkyl" refers to an alkyl group which is  
08 generally derived from polyolefins which are polymers or  
09 copolymers of mono-olefins, particularly 1-mono-olefins,  
10 such as ethylene, propylene, butylene, and the like.  
11 Preferably, the mono-olefin employed will have 2 to about  
12 24 carbon atoms, and more preferably, about 3 to 12 carbon  
13 atoms. More preferred mono-olefins include propylene,  
14 butylene, particularly isobutylene, 1-octene and 1-decene.  
15 Polyolefins prepared from such mono-olefins include  
16 polypropylene, polybutene, especially polyisobutene, and the  
17 polyalphaolefins produced from 1-octene and 1-decene.

18

19 The term "fuel" or "hydrocarbon fuel" refers to normally  
20 liquid hydrocarbons having boiling points in the range of  
21 gasoline and diesel fuels.

22

### 23 General Synthetic Procedures

24

25 The polyalkylphenoxyalkyl aromatic esters employed in this  
26 invention may be prepared by the following general methods  
27 and procedures. It should be appreciated that where typical  
28 or preferred process conditions (e.g., reaction  
29 temperatures, times, mole ratios of reactants, solvents,  
30 pressures, etc.) are given, other process conditions may  
31 also be used unless otherwise stated. Optimum reaction  
32 conditions may vary with the particular reactants or  
33 solvents used, but such conditions can be determined by one  
34 skilled in the art by routine optimization procedures.

01 Those skilled in the art will also recognize that it may be  
02 necessary to block or protect certain functional groups  
03 while conducting the following synthetic procedures. In  
04 such cases, the protecting group will serve to protect the  
05 functional group from undesired reactions or to block its  
06 undesired reaction with other functional groups or with the  
07 reagents used to carry out the desired chemical  
08 transformations. The proper choice of a protecting group  
09 for a particular functional group will be readily apparent  
10 to one skilled in the art. Various protecting groups and  
11 their introduction and removal are described, for example,  
12 in T. W. Greene and P. G. M. Wuts, *Protective Groups in*  
13 *Organic Synthesis*, Second Edition, Wiley, New York, 1991,  
14 and references cited therein.

15  
16 In the present synthetic procedures, a hydroxyl group will  
17 preferably be protected, when necessary, as the benzyl or  
18 tert-butyldimethylsilyl ether. Introduction and removal of  
19 these protecting groups is well described in the art. Amino  
20 groups may also require protection and this may be  
21 accomplished by employing a standard amino protecting group,  
22 such as a benzyloxycarbonyl or a trifluoroacetyl group.  
23 Additionally, as will be discussed in further detail  
24 hereinbelow, the aromatic esters employed in this invention  
25 having an amino group on the aromatic moiety will generally  
26 be prepared from the corresponding nitro derivative.  
27 accordingly, in many of the following procedures, a nitro  
28 group will serve as a protecting group for the amino moiety.

29  
30 Moreover, the aromatic ester compounds employed in this  
31 invention having a  $-\text{CH}_2\text{NH}_2$  group on the aromatic moiety will  
32 generally be prepared from the corresponding cyano  
33 derivative,  $-\text{CN}$ . Thus, in many of the following procedures,  
34



01 a cyano group will serve as a protecting group for the  
02  $-\text{CH}_2\text{NH}_2$  moiety.

03

04 Synthesis

05

06 The polyalkylphenoxyalkyl aromatic esters employed in the  
07 present invention may be prepared by a process which  
08 initially involves hydroxyalkylation of a polyalkylphenol of  
09 the formula:

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(II)

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15 wherein R<sub>4</sub> is as defined herein, with an alkylene carbonate  
16 of the formula:

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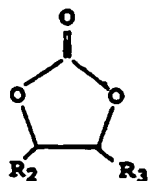
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(III)

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24 wherein R<sub>2</sub> and R<sub>3</sub> are as defined herein, in the presence of  
25 a catalytic amount of an alkali metal hydride or hydroxide,  
26 or alkali metal salt, to provide a polyalkylphenoxyalkanol  
27 of the formula:

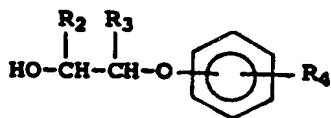
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(IV)

33 wherein R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> are as defined herein.

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01 The polyalkylphenols of formula II are well known materials  
02 and are typically prepared by the alkylation of phenol with  
03 the desired polyolefin or chlorinated polyolefin. A further  
04 discussion of polyalkylphenols can be found, for example, in  
05 U.S. Patent No. 4,744,921 and U.S. Patent No. 5,300,701.

06  
07 Accordingly, the polyalkylphenols of formula II may be  
08 prepared from the corresponding olefins by conventional  
09 procedures. For example, the polyalkylphenols of formula II  
10 above may be prepared by reacting the appropriate olefin or  
11 olefin mixture with phenol in the presence of an alkylating  
12 catalyst at a temperature of from about 25°C. to 150°C., and  
13 preferably 30°C. to 100°C. either neat or in an essentially  
14 inert solvent at atmospheric pressure. A preferred  
15 alkylating catalyst is boron trifluoride. Molar ratios of  
16 reactants may be used. Alternatively, molar excesses of  
17 phenol can be employed, i.e., 2 to 3 equivalents of phenol  
18 for each equivalent of olefin with unreacted phenol  
19 recycled. The latter process maximizes monoalkylphenol.  
20 Examples of inert solvents include heptane, benzene,  
21 toluene, chlorobenzene and 250 thinner which is a mixture of  
22 aromatics, paraffins and naphthenes.

23  
24 The polyalkyl substituent on the polyalkylphenols employed  
25 in the invention is generally derived from polyolefins which  
26 are polymers or copolymers of mono-olefins, particularly  
27 1-mono-olefins, such as ethylene, propylene, butylene, and  
28 the like. Preferably, the mono-olefin employed will have 2  
29 to about 24 carbon atoms, and more preferably, about 3 to  
30 12 carbon atoms. More preferred mono-olefins include  
31 propylene, butylene, particularly isobutylene, 1-octene and  
32 1-decene. Polyolefins prepared from such mono-olefins  
33 include polypropylene, polybutene, especially polyisobutene,  
34

01 and the polyalphaolefins produced from 1-octene and  
02 1-decene.

03

04 The preferred polyisobutenes used to prepare the presently  
05 employed polyalkylphenols are polyisobutenes which comprise  
06 at least about 20% of the more reactive methylvinylidene  
07 isomer, preferably at least 50% and more preferably at least  
08 70%. Suitable polyisobutenes include those prepared using  
09  $\text{BF}_3$  catalysts. The preparation of such polyisobutenes in  
10 which the methylvinylidene isomer comprises a high  
11 percentage of the total composition is described in U.S.  
12 Patent Nos. 4,152,499 and 4,605,808. Such polyisobutenes,  
13 known as "reactive" polyisobutenes, yield high molecular  
14 weight alcohols in which the hydroxyl group is at or near  
15 the end of the hydrocarbon chain. Examples of suitable  
16 polyisobutenes having a high alkylvinylidene content include  
17 Ultravis 30, a polyisobutene having a number average  
18 molecular weight of about 1300 and a methylvinylidene  
19 content of about 74%, and Ultravis 10, a polyisobutene  
20 having a number average molecular weight of about 950 and a  
21 methylvinylidene content of about 76%, both available from  
22 British Petroleum.

23

24 The alkylene carbonates of formula III are known compounds  
25 which are available commercially or can be readily prepared  
26 using conventional procedures. Suitable alkylene carbonates  
27 include ethylene carbonate, propylene carbonate,  
28 1,2-butylene carbonate, 2,3-butylene carbonate, and the  
29 like. A preferred alkylene carbonate is ethylene carbonate.

30

31 The catalyst employed in the reaction of the polyalkylphenol  
32 and alkylene carbonate may be any of the well known  
33 hydroxyalkylation catalysts. Typical hydroxyalkylation  
34 catalysts include alkali metal hydrides, such as lithium

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01 hydride, sodium hydride and potassium hydride, alkali metal  
02 hydroxides, such as sodium hydroxide and potassium  
03 hydroxide, and alkali metal salts, for example, alkali metal  
04 halides, such as sodium chloride and potassium chloride, and  
05 alkali metal carbonates, such as sodium carbonate and  
06 potassium carbonate. The amount of catalyst employed will  
07 generally range from about 0.01 to 1.0 equivalent,  
08 preferably from about 0.05 to 0.3 equivalent.

09  
10 The polyalkylphenol and alkylene carbonate are generally  
11 reacted in essentially equivalent amounts in the presence of  
12 the hydroxyalkylation catalyst at a temperature in the range  
13 of about 100°C. to 210°C., and preferably from about 150°C.  
14 to about 170°C. The reaction may take place in the presence  
15 or absence of an inert solvent.

16  
17 The time of reaction will vary depending on the particular  
18 alkylphenol and alkylene carbonate reactants, the catalyst  
19 used and the reaction temperature. Generally, the reaction  
20 time will range from about two hours to about five hours.  
21 The progress of the reaction is typically monitored by the  
22 evolution of carbon dioxide. At the completion of the  
23 reaction, the polyalkylphenoxyalkanol product is isolated  
24 using conventional techniques.

25  
26 The hydroxyalkylation reaction of phenols with alkylene  
27 carbonates is well known in the art and is described, for  
28 example, in U.S. Patent Nos. 2,987,555; 2,967,892; 3,283,030  
29 and 4,341,905.

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01 Alternatively, the polyalkylphenoxyalkanol product of  
02 formula IV may be prepared by reacting the polyalkylphenol  
03 of formula II with an alkylene oxide of the formula:



09 wherein R<sub>2</sub> and R<sub>3</sub> are as defined herein, in the presence of  
10 a hydroxyalkylation catalyst as described above.  
11 Suitable alkylene oxides of formula V include ethylene  
12 oxide, propylene oxide, 1,2-butylene oxide, 2,3-butylene  
13 oxide, and the like. A preferred alkylene oxide is ethylene  
14 oxide.

15  
16 In a manner similar to the reaction with alkylene carbonate,  
17 the polyalkylphenol and alkylene oxide are reacted in  
18 essentially equivalent or equimolar amounts in the presence  
19 of 0.01 to 1.0 equivalent of a hydroxyalkylation catalyst,  
20 such as sodium or potassium hydride, at a temperature in the  
21 range of about 30°C. to about 150°C., for about 2 to about  
22 24 hours. The reaction may be conducted in the presence or  
23 absence of a substantially anhydrous inert solvent.  
24 Suitable solvents include toluene, xylene, and the like.  
25 Generally, the reaction conducted at a pressure sufficient  
26 to contain the reactants and any solvent present, typically  
27 at atmospheric or higher pressure. Upon completion of the  
28 reaction, the polyalkylphenoxyalkanol is isolated by  
29 conventional procedures.

30  
31 The polyalkylphenoxyalkanol of formula IV is subsequently  
32 reacted with a substituted benzoic acid of formula VI to  
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01 provide the aromatic ester compounds of formula I. This  
 02 reaction can be represented as follows:

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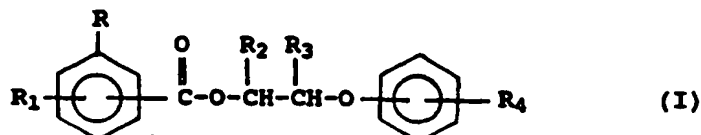
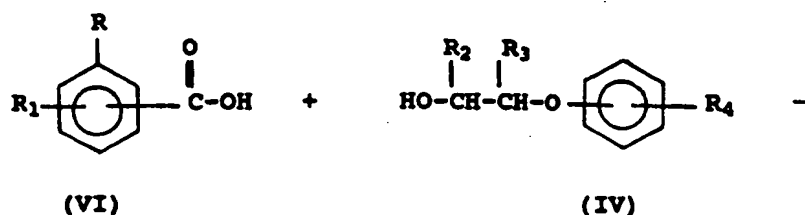
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wherein R, R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> are as defined herein, and wherein any hydroxy or amino substituent on the substituted benzoic acid of formula VI is preferably protected with a suitable protecting group, for example, a benzyl or nitro group, respectively. Moreover, a -CH<sub>2</sub>NH<sub>2</sub> substituent on the aromatic ring will preferably be protected by the use of a cyano group, CN.

This reaction is typically conducted by contacting a polyalkylphenoxyalkanol of formula IV with about 0.25 to about 1.5 molar equivalents of the corresponding substituted and protected benzoic acid of formula VI in the presence of an acidic catalyst at a temperature in the range of about 70°C. to about 160°C. for about 0.5 to about 48 hours.

Suitable acid catalysts for this reaction include p-toluene sulfonic acid, methanesulfonic acid and the like.

Optionally, the reaction can be conducted in the presence of an inert solvent, such as benzene, toluene and the like.

The water generated by this reaction is preferably removed

01 during the course of the reaction, for example, by  
02 azeotropic distillation.

03

04 The substituted benzoic acids of formula VI are generally  
05 known compounds and can be prepared from known compounds  
06 using conventional procedures or obvious modifications  
07 thereof. Representative acids suitable for use as starting  
08 materials include, for example, 2-aminobenzoic acid  
09 (anthranilic acid), 3-aminobenzoic acid, 4-aminobenzoic  
10 acid, 3-amino-4-hydroxybenzoic acid,  
11 4-amino-3-hydroxybenzoic acid, 2-nitrobenzoic acid,  
12 3-nitrobenzoic acid, 4-nitrobenzoic acid,  
13 3-hydroxy-4-nitrobenzoic acid, 4-hydroxy-3-nitrobenzoic  
14 acid. When the R substituent is  $-\text{CH}_2-\text{NR}_5\text{R}_6$ , suitable  
15 starting materials include 4-cyanobenzoic acid and  
16 3-cyanobenzoic acid.

17

18 Preferred substituted benzoic acids include 3-nitrobenzoic  
19 acid, 4-nitrobenzoic acid, 3-hydroxy-4-nitrobenzoic acid,  
20 4-hydroxy-3-nitrobenzoic acid, 3-cyanobenzoic acid and  
21 4-cyanobenzoic acid.

22

23 The compounds of formula I or their suitably protected  
24 analogs also can be prepared by reacting the  
25 polyalkylphenoxyalkanol of formula IV with an acid halide of  
26 the substituted benzoic acid of formula VI such as an acid

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01 chloride or acid bromide. This can be represented by the  
 02 following reaction equation:

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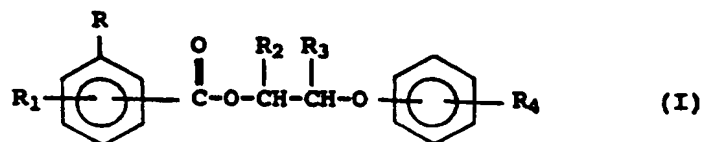
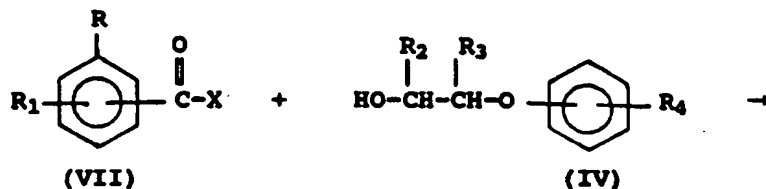
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15 wherein X is halide, typically chloride or bromide, and R,  
 16 R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> are as defined herein above, and wherein  
 17 any hydroxy or amino substituents on the acid halide of  
 18 formula VII are preferably protected with a suitable  
 19 protection group, for example, benzyl or nitro,  
 20 respectively. Also, when R is —CH<sub>2</sub>NR<sub>5</sub>R<sub>6</sub>, a suitable  
 21 starting material is a cyanobenzoyl halide.

22

23 Typically, this reaction is conducted by contacting the  
 24 polyalkylphenoxyalkanol of formula IV with about 0.9 to  
 25 about 1.5 molar equivalents of the acid halide of  
 26 formula VII in an inert solvent, such as, for example,  
 27 toluene, dichloromethane, diethyl ether, and the like, at a  
 28 temperature in the range of about 25°C. to about 150°C. The  
 29 reaction is generally complete in about 0.5 to about  
 30 48 hours. Preferably, the reaction is conducted in the  
 31 presence of a sufficient amount of an amine capable of  
 32 neutralizing the acid generated during the reaction, such  
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01 as, for example, triethylamine, di(isopropyl)ethylamine,  
02 pyridine or 4-dimethylaminopyridine.

03

04 When the benzoic acids of formula VI or acid halides of  
05 formula VII contain a hydroxyl group, protection of the  
06 aromatic hydroxyl groups may be accomplished using  
07 well-known procedures. The choice of a suitable protecting  
08 group for a particular hydroxybenzoic carboxylic acid will  
09 be apparent to those skilled in the art. Various protecting  
10 groups, and their introduction and removal, are described,  
11 for example, in T. W. Greene and P. G. M. Wuts, *Protective*  
12 *Groups in Organic Synthesis*, Second Edition, Wiley,  
13 New York, 1991, and references cited therein.

14

15 After completion of the esterification, deprotection of the  
16 aromatic hydroxyl group can also be accomplished using  
17 conventional procedures. Appropriate conditions for this  
18 deprotection step will depend upon the protecting group(s)  
19 utilized in the synthesis and will be readily apparent to  
20 those skilled in the art. For example, benzyl protecting  
21 groups may be removed by hydrogenolysis under 1 to about  
22 4 atmospheres of hydrogen in the presence of a catalyst,  
23 such as palladium on carbon. Typically, this deprotection  
24 reaction is conducted in an inert solvent, preferably a  
25 mixture of ethyl acetate and acetic acid, at a temperature  
26 of from about 0°C. to about 40°C. for about 1 to about  
27 24 hours.

28

29 When the benzoic acids of formula VI or acyl halides of  
30 formula VII have a free amino group ( $-NH_2$ ) on the phenyl  
31 moiety, it is generally desirable to first prepare the  
32 corresponding nitro compound (i.e., where R and/or  $R_1$  is a  
33 nitro group) using the above-described synthetic procedures,  
34 including preparation of the acyl halides, and then reduce

01 the nitro group to an amino group using conventional  
02 procedures. Aromatic nitro groups may be reduced to amino  
03 groups using a number of procedures that are well known in  
04 the art. For example, aromatic nitro groups may be reduced  
05 under catalytic hydrogenation conditions; or by using a  
06 reducing metal, such as zinc, tin, iron and the like, in the  
07 presence of an acid, such as dilute hydrochloric acid.  
08 Generally, reduction of the nitro group by catalytic  
09 hydrogenation is preferred. Typically, this reaction is  
10 conducted using about 1 to 4 atmospheres of hydrogen and a  
11 platinum or palladium catalyst, such as palladium on carbon.  
12 The reaction is typically carried out at a temperature of  
13 about 0°C. to about 100°C. for about 1 to 24 hours in an  
14 inert solvent, such as ethanol, ethyl acetate and the like.  
15 Hydrogenation of aromatic nitro groups is discussed in  
16 further detail in, for example, P. N. Rylander, *Catalytic*  
17 *Hydrogenation in Organic Synthesis*, pp. 113-137, Academic  
18 Press (1979); and *Organic Synthesis, Collective Vol. I*,  
19 Second Edition, pp. 240-241, John Wiley & Sons, Inc. (1941);  
20 and references cited therein.

21  
22 Likewise, when the benzoic acids of formula VI or acyl  
23 halides of formula VII contain a  $-\text{CH}_2\text{NH}_2$  group on the phenyl  
24 moiety, it is generally desirable to first prepare the  
25 corresponding cyano compounds (i.e., where R and/or  $\text{R}_1$  is a  
26  $-\text{CN}$  group), and then reduce the cyano group to a  $-\text{CH}_2\text{NH}_2$   
27 group using conventional procedures. Aromatic cyano groups  
28 may be reduced to  $-\text{CH}_2\text{NH}_2$  groups using procedures well  
29 known in the art. For example, aromatic cyano groups may be  
30 reduced under catalytic hydrogenation conditions similar to  
31 those described above for reduction of aromatic nitro groups  
32 to amino groups. Thus, this reaction is typically conducted  
33 using about 1 to 4 atmospheres of hydrogen and a platinum or  
34

01 palladium catalyst, such as palladium on carbon. Another  
02 suitable catalyst is a Lindlar catalyst, which is palladium  
03 on calcium carbonate. The hydrogenation may be carried out  
04 at temperatures of about 0°C. to about 100°C. for about 1 to  
05 24 hours in an inert solvent such as ethanol, ethyl acetate,  
06 and the like. Hydrogenation of aromatic cyano groups is  
07 further discussed in the references cited above for  
08 reduction of aromatic nitro groups.

09  
10 The acyl halides of formula VII can be prepared by  
11 contacting the corresponding benzoic acid compound of  
12 formula VI with an inorganic acid halide, such as thionyl  
13 chloride, phosphorous trichloride, phosphorous tribromide,  
14 or phosphorous pentachloride; or with oxalyl chloride.  
15 Typically, this reaction will be conducted using about 1 to  
16 5 molar equivalents of the inorganic acid halide or oxalyl  
17 chloride, either neat or in an inert solvent, such as  
18 diethyl ether, at a temperature in the range of about 20°C.  
19 to about 80°C. for about 1 to about 48 hours. A catalyst,  
20 such as *N,N*-dimethylformamide, may also be used in this  
21 reaction. Again it is preferred to first protect any  
22 hydroxy or amino substituents before converting the benzoic  
23 acid to the acyl halide.

24

25 The Poly(oxyalkylene) Amine

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27 The poly(oxyalkylene) amine component of the present fuel  
28 additive composition is a poly(oxyalkylene) amine having at  
29 least one basic nitrogen atom and a sufficient number of  
30 oxyalkylene units to render the poly(oxyalkylene) amine  
31 soluble in hydrocarbons boiling in the gasoline or diesel  
32 range.

33

34

01 Preferably, such poly(oxyalkylene) amines will also be of  
02 sufficient molecular weight so as to be nonvolatile at  
03 normal engine intake valve operating temperatures, which are  
04 generally in the range of about 200°C to 250°C.

05  
06 Generally, the poly(oxyalkylene) amines suitable for use in  
07 the present invention will contain at least about  
08 5 oxyalkylene units, preferably about 5 to 100, more  
09 preferably about 8 to 100, and even more preferably about 10  
10 to 100. Especially preferred poly(oxyalkylene) amines will  
11 contain about 10 to 25 oxyalkylene units.

12  
13 The molecular weight of the presently employed  
14 poly(oxyalkylene) amines will generally range from about 500  
15 to about 10,000, preferably from about 500 to about 5,000.

16  
17 Suitable poly(oxyalkylene) amine compounds for use in the  
18 present invention include hydrocarbyl poly(oxyalkylene)  
19 polyamines as disclosed, for example, in U.S. Patent  
20 No. 4,247,301, issued January 27, 1981 to Honnen, the  
21 disclosure of which is incorporated herein by reference.  
22 These compounds are hydrocarbyl poly(oxyalkylene) polyamines  
23 wherein the poly(oxyalkylene) moiety comprises at least one  
24 hydrocarbyl-terminated poly(oxyalkylene) chain of 2 to  
25 5 carbon atom oxyalkylene units, and wherein the  
26 poly(oxyalkylene) chain is bonded through a terminal carbon  
27 atom to a nitrogen atom of a polyamine having from 2 to  
28 about 12 amine nitrogen atoms and from 2 to about 40 carbon  
29 atoms with a carbon-to-nitrogen ratio between about 1:1 and  
30 10:1. The hydrocarbyl group on these hydrocarbyl  
31 poly(oxyalkylene) polyamines will contain from about 1 to  
32 30 carbon atoms. These compounds generally have molecular  
33 weights in the range of about 500 to 10,000, preferably from  
34

01 about 500 to 5,000 and more preferably from about 800 to  
02 5,000.

03  
04 The above-described hydrocarbyl poly(oxyalkylene) polyamines  
05 are prepared by conventional procedures known in the art, as  
06 taught, for example, in U.S. Patent No. 4,247,301.

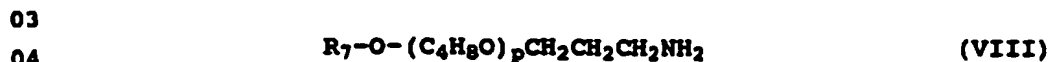
07  
08 Other poly(oxyalkylene) amines suitable for use in the  
09 present invention are the poly(oxyalkylene) polyamines  
10 wherein the poly(oxyalkylene) moiety is connected to the  
11 polyamine moiety through an oxyalkylene hydroxy-type linkage  
12 derived from an epihalohydrin, such as epichlorohydrin or  
13 epibromohydrin. This type of poly(oxyalkylene) amine having  
14 an epihalohydrin-derived linkage is described, for example,  
15 in U.S. Patent No. 4,261,704, issued April 14, 1981 to  
16 Langdon, the disclosure of which is incorporated herein by  
17 reference.

18  
19 Useful polyamines for preparing the epihalohydrin-derived  
20 poly(oxyalkylene) polyamines include, for example, alkylene  
21 polyamines, polyalkylene polyamines, cyclic amines, such as  
22 piperazines, and amino-substituted amines. The  
23 poly(oxyalkylene) polyamines having an epihalohydrin-derived  
24 linkage between the poly(oxyalkylene) and polyamine moieties  
25 are prepared using known procedures as taught, for example,  
26 in U.S. Patent No. 4,261,704.

27  
28 Another type of poly(oxyalkylene) amine useful in the  
29 present invention is a highly branched alkyl  
30 poly(oxyalkylene) monoamine as described, for example in  
31 U.S. Patent No. 5,094,667, issued March 10, 1992 to  
32 Schilowitz et al., the disclosure of which is incorporated  
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01 herein by reference. These highly branched alkyl  
02 poly(oxyalkylene) monoamines have the general formula:



05 wherein  $R_7$  is a highly branched alkyl group containing from  
06 12 to 40 carbon atoms, preferably an alkyl group having  
07 20 carbon atoms which is derived from a Guerbet condensation  
08 reaction, and  $p$  is a number up to 30, preferably 4 to 8.  
09 The preferred alkyl group is derived from a Guerbet alcohol  
10 containing 20 carbon atoms having the formula:  
11



16 wherein  $R_8$  is a hydrocarbyl chain.

17  
18 The above highly branched alkyl poly(oxyalkylene) monoamines  
19 are prepared by using known methods as disclosed, for  
20 example, in U.S. Patent No. 5,094,667.

21  
22 A preferred class of poly(oxyalkylene) amine for use in the  
23 fuel additive composition of the present invention are  
24 hydrocarbyl poly(oxyalkylene) monoamines as described, for  
25 example, in U.S. Patent No. 5,112,364, issued May 12, 1992  
26 to Rath et al., the disclosure of which is incorporated  
27 herein by reference. As disclosed in U.S. Patent  
28 No. 5,112,364, such poly(oxyalkylene) monoamines may be  
29 prepared by the reductive amination of a phenol-initiated or  
30 alkylphenol-initiated poly(oxyalkylene) alcohol with ammonia  
31 or a primary amine.

32  
33 In addition, the above-mentioned U.S. Patent No. 4,247,301  
34 to Honnen discloses hydrocarbyl poly(oxyalkylene) monoamines

01 which are suitable for use in the present fuel additive  
02 composition. In particular, Example 6 of this patent  
03 describes alkylphenyl poly(oxyalkylene) monoamines prepared  
04 from ammonia and dimethylamine.

05

06 A particularly preferred type of hydrocarbyl  
07 poly(oxyalkylene) monoamine is an alkylphenyl  
08 poly(oxyalkylene) monoamine wherein the poly(oxyalkylene)  
09 moiety contains oxypropylene units or oxybutylene units or  
10 mixtures of oxypropylene and oxybutylene units. Preferably,  
11 the alkyl group on the alkylphenyl moiety is a straight or  
12 branched-chain alkyl of 1 to 24 carbon atoms. An especially  
13 preferred alkylphenyl moiety is tetrapropenylphenyl, that  
14 is, where the alkyl group is a branched-chain alkyl of  
15 12 carbon atoms derived from propylene tetramer.

16

17 A further discussion of the hydrocarbon-substituted  
18 poly(oxyalkylene) moiety on the poly(oxyalkylene) amine  
19 component of the present fuel additive composition is found  
20 hereinbelow.

21

22 Another preferred class of poly(oxyalkylene) amine for use  
23 in the fuel additive composition of the present invention  
24 are hydrocarbyl-substituted poly(oxyalkylene)  
25 aminocarbamates disclosed, for example, in U.S. Patent  
26 Nos. 4,288,612; 4,236,020; 4,160,648; 4,191,537; 4,270,930;  
27 4,233,168; 4,197,409; 4,243,798 and 4,881,945, the  
28 disclosure of each of which are incorporated herein by  
29 reference.

30

31 These hydrocarbyl poly(oxyalkylene) aminocarbamates contain  
32 at least one basic nitrogen atom and have an average  
33 molecular weight of about 500 to 10,000, preferably about  
34 500 to 5,000, and more preferably about 1,000 to 3,000. As

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01 described more fully hereinbelow, these hydrocarbyl  
02 poly(oxyalkylene) aminocarbamates contain (a) a  
03 poly(oxyalkylene) moiety, (b) an amine moiety and (c) a  
04 carbamate connecting group.

05

06 A. The Poly(oxyalkylene) Moiety

07

08 The hydrocarbyl-terminated poly(oxyalkylene) polymers which  
09 are utilized in preparing the hydrocarbyl poly(oxyalkylene)  
10 aminocarbamates employed in the present invention are  
11 monohydroxy compounds, e.g., alcohols, often termed  
12 monohydroxy polyethers, or polyalkylene glycol monocarbyl  
13 ethers, or "capped" poly(oxyalkylene) glycols, and are to be  
14 distinguished from the poly(oxyalkylene) glycols (diols), or  
15 polyols, which are not hydrocarbyl-terminated, i.e., are not  
16 capped. These hydrocarbyl poly(oxyalkylene) alcohols may be  
17 produced by the addition of lower alkylene oxides, such as  
18 ethylene oxide, propylene oxide, butylene oxide, etc. to a  
19 hydroxy compound,  $R_9OH$ , under polymerization conditions,  
20 wherein  $R_9$  is the hydrocarbyl group which caps the  
21 poly(oxyalkylene) chain.

22

23 In the hydrocarbyl poly(oxyalkylene) aminocarbamates  
24 employed in the present invention, the hydrocarbyl group  $R_9$   
25 will generally contain from 1 to about 30 carbon atoms,  
26 preferably from 2 to about 20 carbon atoms and is preferably  
27 aliphatic or aromatic, i.e., an alkyl or alkyl phenyl  
28 wherein the alkyl is a straight or branched-chain of from  
29 1 to about 24 carbon atoms. More preferably,  $R_9$  is  
30 alkylphenyl wherein the alkyl group is a branched-chain of  
31 12 carbon atoms, derived from propylene tetramer, and  
32 commonly referred to as tetrapropenyl.

33

34



01 The oxyalkylene units in the poly(oxyalkylene) moiety  
02 preferably contain from 2 to about 5 carbon atoms but one or  
03 more units of a larger carbon number may also be present.  
04 Generally, each poly(oxyalkylene) polymer contains at least  
05 about 5 oxyalkylene units, preferably about 5 to about  
06 100 oxyalkylene units, more preferably about 8 to about  
07 100 units, even more preferably about 10 to 100 units, and  
08 most preferably 10 to about 25 such units. The  
09 poly(oxyalkylene) moiety of the hydrocarbyl  
10 poly(oxyalkylene) aminocarbamates employed in the present  
11 invention is more fully described and exemplified in U.S.  
12 Patent No. 4,191,537, issued March 4, 1980 to Lewis, the  
13 disclosure of which is incorporated herein by reference.

14  
15 Although the hydrocarbyl group on the hydrocarbyl  
16 poly(oxyalkylene) moiety will preferably contain from 1 to  
17 about 30 carbon atoms, longer hydrocarbyl groups,  
18 particularly longer chain alkyl phenyl groups, may also be  
19 employed. For example, alkylphenyl poly(oxyalkylene)  
20 aminocarbamates wherein the alkyl group contains at least  
21 40 carbon atoms, as described in U.S. Patent No. 4,881,945,  
22 issued November 21, 1989 to Buckley, are also contemplated  
23 for use in the present invention. The alkyl phenyl group on  
24 the aminocarbamates of U.S. Patent No. 4,881,945 will  
25 preferably contain an alkyl group of 50 to 200 carbon atoms,  
26 and more preferably, an alkyl group of 60 to 100 carbon  
27 atoms. These longer chain alkyl groups will generally be  
28 derived from olefin polymers, such as polybutene. The  
29 disclosure of U.S. Patent No. 4,881,945 is incorporated  
30 herein by reference.

31  
32 Also contemplated for use in the present invention are  
33 alkylphenyl poly(oxypropylene) aminocarbamates wherein the  
34 alkyl group is a substantially straight-chain alkyl group.

-32-

01 of about 25 to 50 carbon atoms derived from an alpha olefin  
02 oligomer of C<sub>8</sub> to C<sub>20</sub> alpha olefins, as described in  
03 PCT International Patent Application Publication  
04 No. WO 90/07564, published July 12, 1990, the disclosure of  
05 which is incorporated herein by reference.

06

07 B. The Amine Moiety

08

09 The amine moiety of the hydrocarbyl poly(oxyalkylene)  
10 aminocarbamate is preferably derived from a polyamine having  
11 from 2 to about 12 amine nitrogen atoms and from 2 to about  
12 40 carbon atoms.

13

14 The polyamine is preferably reacted with a hydrocarbyl  
15 poly(oxyalkylene) chloroformate to produce the hydrocarbyl  
16 poly(oxyalkylene) aminocarbamate fuel additive finding use  
17 within the scope of the present invention. The  
18 chloroformate is itself derived from the hydrocarbyl  
19 poly(oxyalkylene) alcohol by reaction with phosgene.

20

21 The polyamine provides the hydrocarbyl poly(oxyalkylene)  
22 aminocarbamate with, on the average, at least about one  
23 basic nitrogen atom per carbamate molecule, i.e., a nitrogen  
24 atom titratable by strong acid. The polyamine preferably  
25 has a carbon-to-nitrogen ratio of from about 1:1 to about  
26 10:1. The polyamine may be substituted with substituents  
27 selected from hydrogen, hydrocarbyl groups of from 1 to  
28 about 10 carbon atoms, acyl groups of from 2 to about  
29 10 carbon atoms, and monoketone, monohydroxy, mononitro,  
30 monocyano, alkyl and alkoxy derivatives of hydrocarbyl  
31 groups of from 1 to 10 carbon atoms. It is preferred that  
32 at least one of the basic nitrogen atoms of the polyamine is  
33 a primary or secondary amino nitrogen. The amine moiety of  
34 the hydrocarbyl poly(oxyalkylene) aminocarbamates employed

-33-

01 in the present invention has been described and exemplified  
02 more fully in U.S. Patent No. 4,191,537.

03

04 A more preferred polyamine for use in preparing the  
05 hydrocarbyl poly(oxyalkylene) aminocarbamates finding use  
06 within the scope of the present invention is a polyalkylene  
07 polyamine, including alkylenediamine, and including  
08 substituted polyamines, e.g., alkyl and hydroxyalkyl-  
09 substituted polyalkylene polyamine. Preferably, the  
10 alkylene group contains from 2 to 6 carbon atoms, there  
11 being preferably from 2 to 3 carbon atoms between the  
12 nitrogen atoms. Examples of such polyamines include  
13 ethylenediamine, diethylenetriamine, triethylenetetramine,  
14 di(trimethylene)triamine, dipropylenetriamine,  
15 tetraethylenepentamine, etc.

16

17 Among the polyalkylene polyamines, polyethylene polyamine  
18 and polypropylene polyamine containing 2 to about 12 amine  
19 nitrogen atoms and 2 to about 24 carbon atoms are especially  
20 preferred and in particular, the lower polyalkylene  
21 polyamines, e.g., ethylenediamine, diethylenetriamine,  
22 propylenediamine, dipropylenetriamine, etc., are most  
23 preferred.

24

25 C. The Aminocarbamate Connecting Group

26

27 The hydrocarbyl poly(oxyalkylene) aminocarbamate employed as  
28 the poly(oxyalkylene) amine component of the fuel additive  
29 composition of the present invention is obtained by linking  
30

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01 the polyamine and the hydrocarbyl poly(oxyalkylene) alcohol  
02 together through a carbamate linkage, i.e.,

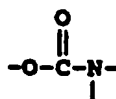
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wherein the oxygen may be regarded as the terminal hydroxyl oxygen of the poly(oxyalkylene) alcohol, the nitrogen is derived from the polyamine and the carbonyl group  $-\text{C}(\text{O})-$ , is preferably provided by a coupling agent, such as phosgene.

In a preferred method of preparation, the hydrocarbyl poly(oxyalkylene) alcohol is reacted with phosgene to produce a chloroformate and the chloroformate is reacted with the polyamine. Since there may be more than one nitrogen atom of the polyamine which is capable of reacting with the chloroformate, the carbamate product may contain more than one hydrocarbyl poly(oxyalkylene) moiety. It is preferred that the hydrocarbyl poly(oxyalkylene) aminocarbamate product contains on the average, about one poly(oxyalkylene) moiety per molecule (i.e., is a monocarbamate), although it is understood that this reaction route may lead to mixtures containing appreciable amounts of di- or higher poly(oxyalkylene) chain substitution on a polyamine containing several reactive nitrogen atoms.

A particularly preferred aminocarbamate is alkylphenyl poly(oxybutylene) aminocarbamate, wherein the amine moiety is derived from ethylene diamine or diethylene triamine. Synthetic methods to avoid higher degrees of substitution, methods of preparation, and other characteristics of the aminocarbamates used in the present invention are more fully described and exemplified in U.S. Patent No. 4,191,537.

Fuel Compositions

01  
02  
03 The fuel additive composition of the present invention will  
04 generally be employed in hydrocarbon fuels to prevent and  
05 control engine deposits, particularly intake valve  
06 deposits. The proper concentration of additive necessary to  
07 achieve the desired deposit control varies depending upon  
08 the type of fuel employed, the type of engine, and the  
09 presence of other fuel additives.  
10  
11 Generally, the present fuel additive composition will be  
12 employed in a hydrocarbon fuel in a concentration ranging  
13 from about 50 to about 5,000 parts per million (ppm) by  
14 weight, preferably from 100 to 2,500 ppm.  
15  
16 In terms of individual components, hydrocarbon fuel  
17 containing the fuel additive composition of this invention  
18 will generally contain about 25 to 2,000 ppm of the  
19 polyalkylphenoxyalkyl aromatic ester component and about 25  
20 to 2,000 ppm of the poly(oxyalkylene) amine component. The  
21 ratio of the polyalkylphenoxyalkyl aromatic ester to  
22 poly(oxyalkylene) amine will generally range from about  
23 0.05:1 to about 5:1, and will preferably be about 2:1 or  
24 less.  
25  
26 The fuel additive composition of the present invention may  
27 be formulated as a concentrate using an inert stable  
28 oleophilic (i.e., dissolves in gasoline) organic solvent  
29 boiling in the range of about 150°F. to 400°F. (about 65°C.  
30 to 205°C.). Preferably, an aliphatic or an aromatic  
31 hydrocarbon solvent is used, such as benzene, toluene,  
32 xylene or higher-boiling aromatics or aromatic thinners.  
33 Aliphatic alcohols containing about 3 to 8 carbon atoms,  
34 such as isopropanol, isobutylcarbinol, n-butanol and the

01 like, in combination with hydrocarbon solvents are also  
02 suitable for use with the present additives. In the  
03 concentrate, the amount of the additive will generally range  
04 from about 10 to about 70 weight percent, preferably 10 to  
05 50 weight percent, more preferably from 20 to 40 weight  
06 percent.

07  
08 In gasoline fuels, other fuel additives may be employed with  
09 the additive composition of the present invention,  
10 including, for example, oxygenates, such as t-butyl methyl  
11 ether, antiknock agents, such as methylcyclopentadienyl  
12 manganese tricarbonyl, and other dispersants/detergents,  
13 such as hydrocarbyl amines, or succinimides. Additionally,  
14 antioxidants, metal deactivators, demulsifiers and  
15 carburetor or fuel injector detergents may be present.

16  
17 In diesel fuels, other well-known additives can be employed,  
18 such as pour point depressants, flow improvers, cetane  
19 improvers, and the like.

20  
21 A fuel-soluble, nonvolatile carrier fluid or oil may also be  
22 used with the fuel additive composition of this invention.  
23 The carrier fluid is a chemically inert hydrocarbon-soluble  
24 liquid vehicle which substantially increases the nonvolatile  
25 residue (NVR), or solvent-free liquid fraction of the fuel  
26 additive composition while not overwhelmingly contributing  
27 to octane requirement increase. The carrier fluid may be a  
28 natural or synthetic fluid, such as mineral oil, refined  
29 petroleum oils, synthetic polyalkanes and alkenes, including  
30 hydrogenated and unhydrogenated polyalphaolefins, and  
31 synthetic polyoxyalkylene-derived fluids, such as those  
32 described, for example, in U.S. Patent No. 4,191,537 to  
33 Lewis, and polyesters, such as those described, for example,  
34 in U.S. Patent Nos. 3,756,793 to Robinson and 5,004,478 to

01 Vogel et al., and in European Patent Application  
02 Nos. 356,726, published March 7, 1990, and 382,159,  
03 published August 16, 1990.

04  
05 These carrier fluids are believed to act as a carrier for  
06 the fuel additive composition of the present invention and  
07 to assist in removing and retarding deposits. The carrier  
08 fluid may also exhibit synergistic deposit control  
09 properties when used in combination with the fuel additive  
10 composition of this invention.

11  
12 The carrier fluids are typically employed in amounts ranging  
13 from about 25 to about 5000 ppm by weight of the hydrocarbon  
14 fuel, preferably from 100 to 3000 ppm of the fuel.  
15 Preferably, the ratio of carrier fluid to deposit control  
16 additive will range from about 0.2:1 to about 10:1, more  
17 preferably from 0.5:1 to 3:1.

18  
19 When employed in a fuel concentrate, carrier fluids will  
20 generally be present in amounts ranging from about 20 to  
21 about 60 weight percent, preferably from 30 to 50 weight  
22 percent.

#### 23 24 PREPARATIONS AND EXAMPLES

25  
26 A further understanding of the invention can be had in the  
27 following nonlimiting Examples. Wherein unless expressly  
28 stated to the contrary, all temperatures and temperature  
29 ranges refer to the Centigrade system and the term "ambient"  
30 or "room temperature" refers to about 20°C. to 25°C. The  
31 term "percent" or "%" refers to weight percent and the term  
32 "mole" or "moles" refers to gram moles. The term  
33 "equivalent" refers to a quantity of reagent equal in moles,  
34 to the moles of the preceding or succeeding reactant recited

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01 in that example in terms of finite moles or finite weight or  
02 volume. Where given, proton-magnetic resonance spectrum  
03 (p.m.r. or n.m.r.) were determined at 300 MHz, signals are  
04 assigned as singlets (s), broad singlets (bs), doublets (d),  
05 double doublets (dd), triplets (t), double triplets (dt),  
06 quartets (q), and multiplets (m), and cps refers to cycles  
07 per second.

08

09

Example 1

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11

Preparation of Polyisobutyl Phenol

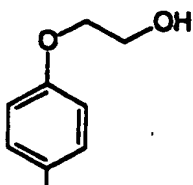
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13 To a flask equipped with a magnetic stirrer, reflux  
14 condenser, thermometer, addition funnel and nitrogen inlet  
15 was added 203.2 grams of phenol. The phenol was warmed to  
16 40°C. and the heat source was removed. Then,  
17 73.5 milliliters of boron trifluoride etherate was added  
18 dropwise. 1040 grams of Ultravis 10 Polyisobutene  
19 (molecular weight 950, 76% methylvinylidene, available from  
20 British Petroleum) was dissolved in 1,863 milliliters of  
21 hexane. The polyisobutene was added to the reaction at a  
22 rate to maintain the temperature between 22°C. to 27°C. The  
23 reaction mixture was stirred for 16 hours at room  
24 temperature. Then, 400 milliliters of concentrated ammonium  
25 hydroxide was added, followed by 2,000 milliliters of  
26 hexane. The reaction mixture was washed with water  
27 (3 X 2,000 milliliters), dried over magnesium sulfate,  
28 filtered and the solvents removed under vacuum to yield  
29 1,056.5 grams of a crude reaction product. The crude  
30 reaction product was determined to contain 80% of the  
31 desired product by proton NMR and chromatography on silica  
32 gel eluting with hexane, followed by hexane: ethylacetate:  
33 ethanol (93:5:2).

34



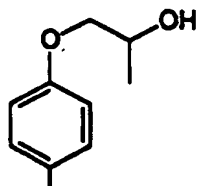
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Example 2Preparation of

PB (molecular weight ~ 950)

1.1 grams of a 35 weight percent dispersion of potassium hydride in mineral oil and 4- polyisobutyl phenol (99.7 grams, prepared as in Example 1) were added to a flask equipped with a magnetic stirrer, reflux condensor, nitrogen inlet and thermometer. The reaction was heated at 130°C for one hour and then cooled to 100°C. Ethylene carbonate (8.6 grams) was added and the mixture was heated at 160°C for 16 hours. The reaction was cooled to room temperature and one milliliter of isopropanol was added. The reaction was diluted with one liter of hexane, washed three times with water and once with brine. The organic layer was dried over anhydrous magnesium sulfate, filtered and the solvents removed *in vacuo* to yield 98.0 grams of the desired product as a yellow oil.

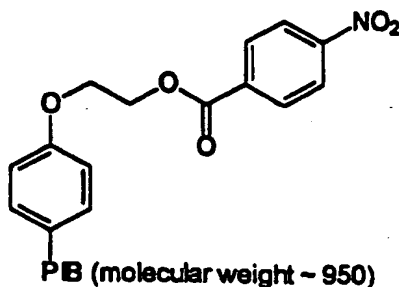
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Example 1Preparation of

PIB (molecular weight ~ 950)

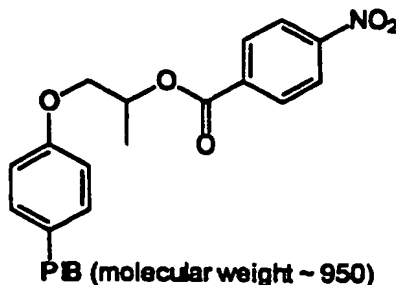
15.1 grams of a 35 weight percent dispersion of potassium hydride in mineral oil and 4- polyisobutyl phenol (1378.5 grams, prepared as in Example 1) were added to a flask equipped with a mechanical stirrer, reflux condensor, nitrogen inlet and thermometer. The reaction was heated at 130°C for one hour and then cooled to 100°C. Propylene carbonate (115.7 milliliters) was added and the mixture was heated at 160°C for 16 hours. The reaction was cooled to room temperature and ten milliliters of isopropanol were added. The reaction was diluted with ten liters of hexane, washed three times with water and once with brine. The organic layer was dried over anhydrous magnesium sulfate, filtered and the solvents removed in vacuo to yield 1301.7 grams of the desired product as a yellow oil.

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Example 4Preparation of

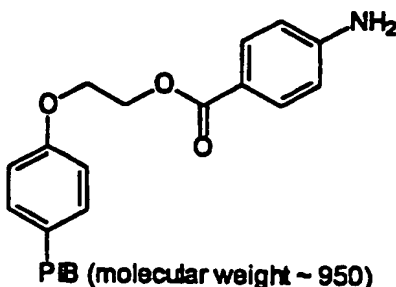
To a flask equipped with a magnetic stirrer, thermometer, Dean-Stark trap, reflux condensor and nitrogen inlet was added 15.0 grams of the alcohol from Example 2, 2.6 grams of 4-nitrobenzoic acid and 0.24 grams of *p*-toluenesulfonic acid. The mixture was stirred at 130°C for sixteen hours, cooled to room temperature and diluted with 200 mL of hexane. The organic phase was washed twice with saturated aqueous sodium bicarbonate followed by once with saturated aqueous sodium chloride. The organic layer was then dried over anhydrous magnesium sulfate, filtered and the solvents removed *in vacuo* to yield 15.0 grams of the desired product as a brown oil. The oil was chromatographed on silica gel, eluting with hexane/ethyl acetate (9:1) to afford 14.0 grams of the desired ester as a yellow oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 8.3 (AB quartet, 4H), 7.25 (d, 2H), 6.85 (d, 2H), 4.7 (t, 2H), 4.3 (t, 2H), 0.7-1.6 (m, 137H).

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Example 5Preparation of

To a flask equipped with a magnetic stirrer, thermometer, Dean-Stark trap, reflux condenser and nitrogen inlet was added 15.0 grams of the alcohol from Example 3, 2.7 grams of 4-nitrobenzoic acid and 0.23 grams of *p*-toluenesulfonic acid. The mixture was stirred at 130°C for sixteen hours, cooled to room temperature and diluted with 200 mL of hexane. The organic phase was washed twice with saturated aqueous sodium bicarbonate followed by once with saturated aqueous sodium chloride. The organic layer was then dried over anhydrous magnesium sulfate, filtered and the solvents removed *in vacuo* to yield 16.0 grams of the desired product as a brown oil. The oil was chromatographed on silica gel, eluting with hexane/ethyl acetate (8:2) to afford 15.2 grams of the desired ester as a brown oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 8.2 (AB quartet, 4H), 7.25 (d, 2H), 6.85 (d, 2H), 5.55 (hx, 1H), 4.1 (t, 2H), 0.6-1.8 (m, 140H).

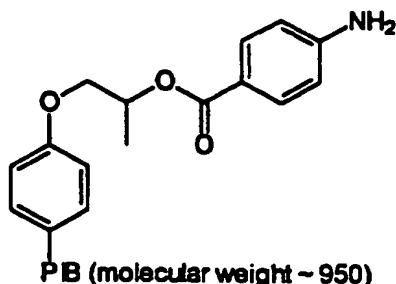
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Example 6Preparation of

A solution of 9.4 grams of the product from Example 4 in 100 milliliters of ethyl acetate containing 1.0 gram of 10% palladium on charcoal was hydrogenolyzed at 35-40 psi for 16 hours on a Parr low-pressure hydrogenator. Catalyst filtration and removal of the solvent in vacuo yield 7.7 grams of the desired product as a yellow oil.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.85 (d, 2H), 7.3 (d, 2H), 6.85 (d, 2H), 6.6 (d, 2H), 4.6 (t, 2H), 4.25 (t, 2H), 4.05 (bs, 2H), 0.7-1.6 (m, 137H).

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Example 7Preparation of

A solution of 15.2 grams of the product from Example 5 in 200 milliliters of ethyl acetate containing 1.0 gram of 10% palladium on charcoal was hydrogenolyzed at 35-40 psi for 16 hours on a Parr low-pressure hydrogenator. Catalyst filtration and removal of the solvent in vacuo yield 15.0 grams of the desired product as a brown oil.

$^1\text{H}$  NMR ( $\text{CDCl}_3/\text{D}_2\text{O}$ )  $\delta$  7.85 (d, 2H), 7.25 (d, 2H), 6.85 (d, 2H), 6.6 (d, 2H), 5.4 (hx, 1H), 3.8-4.2 (m, 4H), 0.6-1.8 (m, 140H).

Example 8

Preparation of Dodecylphenoxy  
Poly(oxybutylene)poly(oxypropylene) Amine

A dodecylphenoxypoly(oxybutylene)poly(oxypropylene) amine was prepared by the reductive amination with ammonia of the random copolymer poly(oxyalkylene) alcohol, dodecylphenoxy poly(oxybutylene)poly(oxypropylene) alcohol, wherein the alcohol has an average molecular weight of about 1598. The poly(oxyalkylene) alcohol was prepared from dodecylphenol

-45-

01 using a 75/25 weight/weight ratio of butylene oxide and  
02 propylene oxide, in accordance with the procedures described  
03 in U.S. Patent Nos. 4,191,537; 2,782,240 and 2,841,479, as  
04 well as in Kirk-Othmer, "Encyclopedia of Chemical  
05 Technology", 4th edition, Volume 19, 1996, page 722. The  
06 reductive amination of the poly(oxyalkylene) alcohol was  
07 carried out using conventional techniques as described in  
08 U.S. Patent Nos. 5,112,364; 4,609,377 and 3,440,029.

09

10

Example 9

11

12

Single-Cylinder Engine Test

13

14 The test compounds were blended in gasoline and their  
15 deposit reducing capacity determined in an ASTM/CFR  
16 single-cylinder engine test.

17

18 A Waukesha CFR single-cylinder engine was used. Each run  
19 was carried out for 15 hours, at the end of which time the  
20 intake valve was removed, washed with hexane and weighed.  
21 The previously determined weight of the clean valve was  
22 subtracted from the weight of the valve at the end of the  
23 run. The differences between the two weights is the weight  
24 of the deposit. A lesser amount of deposit indicates a  
25 superior additive. The operating conditions of the test  
26 were as follows: water jacket temperature 200°F; intake  
27 manifold vacuum of 12 in. Hg, air-fuel ratio of 12, ignition  
28 spark timing of 40 BTC; engine speed is 1800 rpm; the  
29 crankcase oil is a commercial 30W oil.

30

31 The amount of carbonaceous deposit in milligrams on the  
32 intake valves is reported for each of the test compounds in  
33 Table I.

34

-46-

**TABLE I****Intake Valve Deposit Weight  
(in milligrams)**

<b>Sample<sup>1</sup></b>	<b>Run 1</b>	<b>Run 2</b>	<b>Average</b>
<b>Base Fuel</b>	<b>354.9</b>	<b>333.5</b>	<b>344.2</b>
<b>Example 4</b>	<b>169.0</b>	<b>178.0</b>	<b>173.5</b>
<b>Example 6</b>	<b>13.4</b>	<b>12.2</b>	<b>12.8</b>

<sup>1</sup>At 150 parts per million actives (ppma).

The base fuel employed in the above single-cylinder engine tests was a regular octane unleaded gasoline containing no fuel detergent. The test compounds were admixed with the base fuel to give a concentration of 150 ppma (parts per million actives).

The data in Table I illustrates the significant reduction in intake valve deposits provided by the aromatic ester component of the present invention (Examples 4 and 6) compared to the base fuel.



Example 10Multicylinder Engine Test

The fuel additive composition of the present invention was tested in a laboratory multicylinder engine to evaluate their intake valve and combustion chamber deposit control performance. The test engine was a 2.3 liter, port fuel injected, 4-cylinder single overhead cam engine manufactured by Ford Motor Company. The major engine dimensions are set forth in Table II.

Table II

Engine Dimensions

Bore	9.60 cm
Stroke	7.94 cm
Displacement Volume	2.30 liter
Compression Ratio	9.50:1

The test engine was operated for 60 hours (24 hours a day) on a test cycle developed by the Coordinating Research Council (CRC). The cycle for engine operation during the test is set forth in Table III.

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Table III

Engine Operating Cycle

Stage	Length of Time <sup>1</sup> (Min:Sec)	Engine Speed [RPM]	Manifold Absolute Pressure [mm Hg]
1	4:00	2000 ± 10	230 ± 10
2	8:00	2800 ± 10	540 ± 10

<sup>1</sup> All stages include a 30 second transition ramp.

All of the test runs were made with the same base gasoline, which was representative of commercial unleaded fuel. The results are set forth in Table IV.

Table IV

Multicylinder Engine Test Results

Sample	Conc. (ppma)	Intake Valve Deposits, mg	Combustion Chamber Deposits, mg
Base Fuel	---	521	945
Aromatic Ester/ Carrier Fluid <sup>1</sup>	50/50	657	1262
Aromatic Ester/ Poly(oxyalkylene) Amine <sup>2</sup>	50/50	262	1087

<sup>1</sup> Mixture of 50 ppm of 4-polyisobutylphenoxyethyl para-aminobenzoate prepared as described in Example 6 and 50 ppm of a dodecylphenoxypoly(oxybutylene) alcohol carrier fluid.

<sup>2</sup> Mixture of 50 ppm of 4-polyisobutylphenoxyethyl para-aminobenzoate and 50 ppm of dodecylphenoxy poly(oxybutylene)poly(oxypropylene) amine prepared as described in Example 8.

The base fuel employed in the above multicylinder engine tests contained no fuel detergent. The test compounds were admixed with the base fuel at the indicated concentrations.

The data in Table IV demonstrates that the combination of a polyalkylphenoxyalkyl aromatic ester and a poly(oxyalkylene) amine has a synergistic effect and gives significantly better intake valve deposit control than the aromatic ester component with a carrier fluid. Moreover, the data in Table IV further demonstrates that the combination of aromatic ester and poly(oxyalkylene) amine produces fewer combustion chamber deposits than the aromatic ester component with a carrier fluid.

01 WHAT IS CLAIMED IS:

02

03 1. A fuel additive composition comprising:

04

05 (a) an aromatic ester compound of the formula:

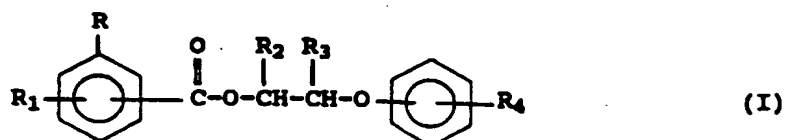
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or a fuel soluble salt thereof, wherein R is hydroxy, nitro or  $-(CH_2)_x-NR_5R_6$ , wherein  $R_5$  and  $R_6$  are independently hydrogen or lower alkyl having 1 to 6 carbon atoms and x is 0 or 1;

16

17

18

19

$R_1$  is hydrogen, hydroxy, nitro or  $-NR_7R_8$ , wherein  $R_7$  and  $R_8$  are independently hydrogen or lower alkyl having 1 to 6 carbon atoms;

20

21

22

$R_2$  and  $R_3$  are independently hydrogen or lower alkyl having 1 to 6 carbon atoms; and

23

24

25

26

$R_4$  is a polyalkyl group having an average molecular weight in the range of about 450 to 5,000; and

27

28

29

30

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34

(b) a poly(oxyalkylene) amine having at least one basic nitrogen atom and a sufficient number of oxyalkylene units to render the poly(oxyalkylene) amine soluble in hydrocarbons boiling in the gasoline or diesel fuel range.

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- 01 2. The fuel additive composition according to Claim 1,  
02 wherein R is nitro, amino or  $-\text{CH}_2\text{NH}_2$ .
- 03 3. The fuel additive composition according to Claim 2,  
04 wherein R is amino, or  $-\text{CH}_2\text{NH}_2$ .  
05
- 06 4. The fuel additive composition according to Claim 3,  
07 wherein R is amino.  
08
- 09 5. The fuel additive composition according to Claim 1,  
10 wherein  $\text{R}_1$  is hydrogen, hydroxy, nitro or amino.
- 11 6. The fuel additive composition according to Claim 5,  
12 wherein  $\text{R}_1$  is hydrogen or hydroxy.  
13
- 14 7. The fuel additive composition according to Claim 6,  
15 wherein  $\text{R}_1$  is hydrogen.  
16
- 17 8. The fuel additive composition according to Claim 1,  
18 wherein one of  $\text{R}_2$  and  $\text{R}_3$  is hydrogen or lower alkyl of  
19 1 to 4 carbon atoms, and the other is hydrogen.
- 20 9. The fuel additive composition according to Claim 8,  
21 wherein one of  $\text{R}_2$  and  $\text{R}_3$  is hydrogen, methyl or ethyl,  
22 and the other is hydrogen.  
23
- 24 10. The fuel additive composition according to Claim 9,  
25 wherein  $\text{R}_2$  is hydrogen, methyl or ethyl, and  $\text{R}_3$  is  
26 hydrogen.  
27
- 28 11. The fuel additive composition according to Claim 1,  
29 wherein  $\text{R}_4$  is a polyalkyl group having an average  
30 molecular weight in the range of about 500 to 3,000.  
31  
32  
33  
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- 01  
02  
03 12. The fuel additive composition according to Claim 11,  
04 wherein  $R_4$  is a polyalkyl group having an average  
05 molecular weight in the range of about 700 to 3,000.  
06 13. The fuel additive composition according to Claim 12,  
07 wherein  $R_4$  is a polyalkyl group having an average  
08 molecular weight in the range of about 900 to 2,500.  
09  
10 14. The fuel additive composition according to Claim 1,  
11 wherein  $R_4$  is a polyalkyl group derived from  
12 polypropylene, polybutene, or a polyalphaolefin  
13 oligomer of 1-octene or 1-decene.  
14  
15 15. The fuel additive composition according to Claim 14,  
16 wherein  $R_4$  is a polyalkyl group derived from  
17 polyisobutene.  
18 16. The fuel additive composition according to Claim 15,  
19 wherein the polyisobutene contains at least about 20%  
20 of a methylvinylidene isomer.  
21  
22 17. The fuel additive composition according to Claim 1,  
23 wherein R is amino,  $R_1$ ,  $R_2$  and  $R_3$  are hydrogen and  $R_4$   
24 is a polyalkyl group derived from polyisobutene.  
25  
26 18. The fuel additive composition according to Claim 1,  
27 wherein said poly(oxyalkylene) amine has a molecular  
28 weight in the range of about 500 to about 10,000.  
29 19. The fuel additive composition according to Claim 1,  
30 wherein said poly(oxyalkylene) amine contains at least  
31 about 5 oxyalkylene units.  
32  
33  
34

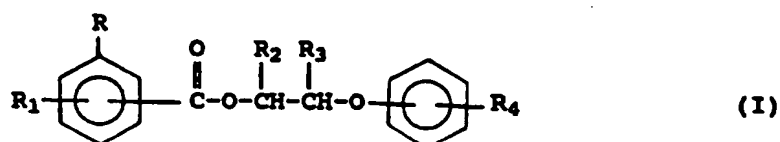
- 01 20. The fuel additive composition according to Claim 1,  
02 wherein said poly(oxyalkylene) amine is a hydrocarbyl  
03 poly(oxyalkylene) polyamine.
- 04 21. The fuel additive composition according to Claim 1,  
05 wherein said poly(oxyalkylene) amine is a hydrocarbyl  
06 poly(oxyalkylene) aminocarbamate.  
07
- 08 22. The fuel additive composition according to Claim 21,  
09 wherein the hydrocarbyl group of said hydrocarbyl  
10 poly(oxyalkylene) aminocarbamate contains from 1 to  
11 about 30 carbon atoms.  
12
- 13 23. The fuel additive composition according to Claim 22,  
14 wherein said hydrocarbyl group of said hydrocarbyl  
15 poly(oxyalkylene) aminocarbamate is an alkylphenyl  
16 group.
- 17 24. The fuel additive composition according to Claim 23,  
18 wherein the alkyl moiety of said alkylphenyl group is  
19 tetrapropenyl.  
20
- 21 25. The fuel additive composition according to Claim 21,  
22 wherein the amine moiety of said hydrocarbyl  
23 poly(oxyalkylene) aminocarbamate is derived from a  
24 polyamine having from 2 to 12 amine nitrogen atoms and  
25 from 2 to 40 carbon atoms.  
26
- 27 26. The fuel additive composition according to Claim 25,  
28 wherein said polyamine is a polyalkylene polyamine  
29 having 2 to 12 amine nitrogen atoms and 2 to 24 carbon  
30 atoms.
- 31 27. The fuel additive composition according to Claim 26,  
32 wherein said polyalkylene polyamine is selected from  
33 the group consisting of ethylenediamine,  
34

- 01 propylenediamine, diethylenetriamine and  
02 dipropylenetriamine.
- 03 28. The fuel additive composition according to Claim 21,  
04 wherein the poly(oxyalkylene) moiety of said  
05 hydrocarbyl poly(oxyalkylene) aminocarbamate is derived  
06 from C<sub>2</sub> to C<sub>5</sub> oxyalkylene units.  
07
- 08 29. The fuel additive composition according to Claim 21,  
09 wherein said hydrocarbyl poly(oxyalkylene)  
10 aminocarbamate is an alkylphenyl poly(oxybutylene)  
11 aminocarbamate, wherein the amine moiety is derived  
12 from ethylenediamine or diethylenetriamine.  
13
- 14 30. The fuel additive composition according to Claim 1,  
15 wherein said poly(oxyalkylene) amine is a hydrocarbyl  
16 poly(oxyalkylene) monoamine.
- 17 31. The fuel additive composition according to Claim 30,  
18 wherein said hydrocarbyl poly(oxyalkylene) monoamine is  
19 an alkylphenyl poly(oxyalkylene) monoamine, wherein the  
20 poly(oxyalkylene) moiety contains oxypropylene units or  
21 oxybutylene units or mixtures thereof.  
22
- 23 32. The fuel additive composition according to Claim 31,  
24 wherein the alkylphenyl group is tetrapropenylphenyl.  
25  
26  
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33. A fuel composition comprising a major amount of hydrocarbons boiling in the gasoline or diesel range and an effective deposit-controlling amount of a fuel additive composition comprising:

(a) an aromatic ester compound of the formula:



or a fuel soluble salt thereof, wherein R is hydroxy, nitro or  $-(\text{CH}_2)_x-\text{NR}_5\text{R}_6$ , wherein  $\text{R}_5$  and  $\text{R}_6$  are independently hydrogen or lower alkyl having 1 to 6 carbon atoms and x is 0 or 1;

$\text{R}_1$  is hydrogen, hydroxy, nitro or  $-\text{NR}_7\text{R}_8$ , wherein  $\text{R}_7$  and  $\text{R}_8$  are independently hydrogen or lower alkyl having 1 to 6 carbon atoms;

$\text{R}_2$  and  $\text{R}_3$  are independently hydrogen or lower alkyl having 1 to 6 carbon atoms; and

$\text{R}_4$  is a polyalkyl group having an average molecular weight in the range of about 450 to 5,000; and

(b) a poly(oxyalkylene) amine having at least one basic nitrogen atom and a sufficient number of oxyalkylene units to render the poly(oxyalkylene)

- 01           amine soluble in hydrocarbons boiling in the  
02           gasoline or diesel fuel range.
- 03           34. The fuel composition according to Claim 33, wherein R  
04           is nitro, amino or  $-\text{CH}_2\text{NH}_2$ .  
05
- 06           35. The fuel composition according to Claim 34, wherein R  
07           is amino, or  $-\text{CH}_2\text{NH}_2$ .  
08
- 09           36. The fuel composition according to Claim 35, wherein R  
10           is amino.
- 11           37. The fuel composition according to Claim 33, wherein  $\text{R}_1$   
12           is hydrogen, hydroxy, nitro or amino.  
13
- 14           38. The fuel composition according to Claim 37, wherein  $\text{R}_1$   
15           is hydrogen or hydroxy.  
16
- 17           39. The fuel composition according to Claim 38, wherein  $\text{R}_1$   
18           is hydrogen.
- 19           40. The fuel composition according to Claim 33, wherein one  
20           of  $\text{R}_2$  and  $\text{R}_3$  is hydrogen or lower alkyl of 1 to 4  
21           carbon atoms, and the other is hydrogen.  
22
- 23           41. The fuel composition according to Claim 40, wherein one  
24           of  $\text{R}_2$  and  $\text{R}_3$  is hydrogen, methyl or ethyl, and the  
25           other is hydrogen.  
26
- 27           42. The fuel composition according to Claim 41, wherein  $\text{R}_2$   
28           is hydrogen, methyl or ethyl, and  $\text{R}_3$  is hydrogen.
- 29           43. The fuel composition according to Claim 33, wherein  $\text{R}_4$   
30           is a polyalkyl group having an average molecular weight  
31           in the range of about 500 to 3,000.  
32  
33  
34

- 01  
02  
03 44. The fuel composition according to Claim 43, wherein R<sub>4</sub>  
04 is a polyalkyl group having an average molecular weight  
05 in the range of about 700 to 3,000.
- 06 45. The fuel composition according to Claim 44, wherein R<sub>4</sub>  
07 is a polyalkyl group having an average molecular weight  
08 in the range of about 900 to 2,500.
- 09  
10 46. The fuel composition according to Claim 33, wherein R<sub>4</sub>  
11 is a polyalkyl group derived from polypropylene,  
12 polybutene, or a polyalphaolefin oligomer of 1-octene  
13 or 1-decene.
- 14  
15 47. The fuel composition according to Claim 46, wherein R<sub>4</sub>  
16 is a polyalkyl group derived from polyisobutene.
- 17 48. The fuel composition according to Claim 47, wherein the  
18 polyisobutene contains at least about 20% of a  
19 methylvinylidene isomer.
- 20  
21 49. The fuel composition according to Claim 33, wherein R  
22 is amino, R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> are hydrogen and R<sub>4</sub> is a  
23 polyalkyl group derived from polyisobutene.
- 24 50. The fuel composition according to Claim 33, wherein the  
25 composition contains from about 25 to about 2,000 parts  
26 per million by weight of said aromatic ester compound  
27 and about 25 to about 2,000 parts per million of said  
28 poly(oxyalkylene) amine.
- 29  
30 51. The fuel composition according to Claim 33, where the  
31 composition further contains from about 25 to about  
32 5,000 parts per million by weight of a fuel-soluble,  
33 nonvolatile carrier fluid.
- 34

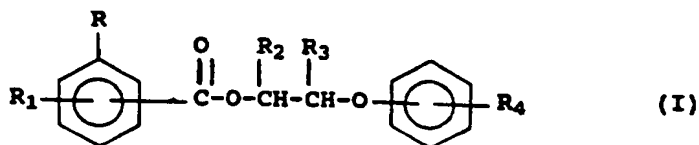
- 01 52. The fuel composition according to Claim 33, wherein  
02 said poly(oxyalkylene) amine is a hydrocarbyl  
03 poly(oxyalkylene) aminocarbamate.
- 04 53. The fuel composition according to Claim 52, wherein the  
05 hydrocarbyl group of said hydrocarbyl poly(oxyalkylene)  
06 aminocarbamate contains from 1 to about 30 carbon  
07 atoms; and wherein the amine moiety of said hydrocarbyl  
08 poly(oxyalkylene) aminocarbamate is derived from a  
09 polyamine having from 2 to 12 amine nitrogen atoms and  
10 from 2 to 40 carbon atoms.  
11
- 12 54. The fuel composition according to Claim 53, wherein  
13 said hydrocarbyl group of said hydrocarbyl  
14 poly(oxyalkylene) aminocarbamate is an alkylphenyl  
15 group; and wherein said polyalkylene polyamine is  
16 selected from the group consisting of ethylenediamine,  
17 propylenediamine, diethylenetriamine and  
18 dipropylenetriamine.  
19
- 20 55. The fuel composition according to Claim 54, wherein the  
21 alkyl moiety of said alkylphenyl group is  
22 tetrapropenyl.
- 23 56. The fuel composition according to Claim 52, wherein  
24 said hydrocarbyl poly(oxyalkylene) aminocarbamate is an  
25 alkylphenyl poly(oxybutylene) aminocarbamate, wherein  
26 the amine moiety is derived from ethylenediamine or  
27 diethylenetriamine.  
28
- 29 57. The fuel composition according to Claim 33, wherein  
30 said poly(oxyalkylene) amine is a hydrocarbyl  
31 poly(oxyalkylene) monoamine.  
32
- 33 58. The fuel composition according to Claim 57, wherein  
34 said hydrocarbyl poly(oxyalkylene) monoamine is an

01 alkylphenyl poly(oxyalkylene) monoamine, wherein the  
 02 poly(oxyalkylene) moiety contains oxypropylene units or  
 03 oxybutylene units or mixtures thereof.

04 59. The fuel composition according to Claim 58, wherein the  
 05 alkylphenyl group is tetrapropenylphenyl.  
 06

07 60. A fuel concentrate comprising an inert stable  
 08 oleophilic organic solvent boiling in the range of from  
 09 about 150°F. to 400°F. and from about 10 to about  
 10 70 weight percent of a fuel additive composition  
 11 comprising:  
 12

13 (a) an aromatic ester compound of the formula:  
 14  
 15  
 16



21 or a fuel soluble salt thereof, wherein R is  
 22 hydroxy, nitro or  $-(CH_2)_x-NR_5R_6$ , wherein  $R_5$  and  $R_6$   
 23 are independently hydrogen or lower alkyl having 1  
 24 to 6 carbon atoms and x is 0 or 1;  
 25

26  $R_1$  is hydrogen, hydroxy, nitro or  $-NR_7R_8$ , wherein  
 27  $R_7$  and  $R_8$  are independently hydrogen or lower  
 28 alkyl having 1 to 6 carbon atoms;  
 29

30  $R_2$  and  $R_3$  are independently hydrogen or lower  
 31 alkyl having 1 to 6 carbon atoms; and  
 32  
 33  
 34

-60-

- 01           R<sub>4</sub> is a polyalkyl group having an average  
02           molecular weight in the range of about 450 to  
03           5,000; and
- 04           (b) a poly (oxyalkylene) amine having at least one  
05           basic nitrogen atom and a sufficient number of  
06           oxyalkylene units to render the poly(oxyalkylene) amine  
07           soluble in hydrocarbons boiling in the gasoline or  
08           diesel fuel range.  
09
- 10   61.   The fuel concentrate according to Claim 60, wherein R  
11       is nitro, amino or -CH<sub>2</sub>NH<sub>2</sub>.  
12
- 13   62.   The fuel concentrate according to Claim 61, wherein R  
14       is amino, or -CH<sub>2</sub>NH<sub>2</sub>.  
15
- 16   63.   The fuel concentrate according to Claim 62, wherein R  
17       is amino.  
18
- 19   64.   The fuel concentrate according to Claim 60, wherein R<sub>1</sub>  
20       is hydrogen, hydroxy, nitro or amino.  
21
- 22   65.   The fuel concentrate according to Claim 64, wherein R<sub>1</sub>  
23       is hydrogen or hydroxy.  
24
- 25   66.   The fuel concentrate according to Claim 65, wherein R<sub>1</sub>  
26       is hydrogen.  
27
- 28   67.   The fuel concentrate according to Claim 60, wherein one  
29       of R<sub>2</sub> and R<sub>3</sub> is hydrogen or lower alkyl of 1 to  
30       4 carbon atoms, and the other is hydrogen.  
31  
32  
33  
34

- 01 68. The fuel concentrate according to Claim 67, wherein one  
02 of R<sub>2</sub> and R<sub>3</sub> is hydrogen, methyl or ethyl, and the  
03 other is hydrogen.  
04
- 05 69. The fuel concentrate according to Claim 68, wherein R<sub>2</sub>  
06 is hydrogen, methyl or ethyl, and R<sub>3</sub> is hydrogen.  
07
- 08 70. The fuel concentrate according to Claim 60, wherein R<sub>4</sub>  
09 is a polyalkyl group having an average molecular weight  
10 in the range of about 500 to 3,000.  
11
- 12 71. The fuel concentrate according to Claim 70, wherein R<sub>4</sub>  
13 is a polyalkyl group having an average molecular weight  
14 in the range of about 700 to 3,000.  
15
- 16 72. The fuel concentrate according to Claim 71, wherein R<sub>4</sub>  
17 is a polyalkyl group having an average molecular weight  
18 in the range of about 900 to 2,500.  
19
- 20 73. The fuel concentrate according to Claim 60, wherein R<sub>4</sub>  
21 is a polyalkyl group derived from polypropylene,  
22 polybutene, or a polyalphaolefin oligomer of 1-octene  
23 or 1-decene.  
24
- 25 74. The fuel concentrate according to Claim 73, wherein R<sub>4</sub>  
26 is a polyalkyl group derived from polyisobutene.  
27
- 28 75. The fuel concentrate according to Claim 74, wherein the  
29 polyisobutene contains at least about 20% of a  
30 methylvinylidene isomer.  
31  
32  
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34

- 01 76. The fuel concentrate according to Claim 60, wherein R  
02 is amino, R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> are hydrogen and R<sub>4</sub> is a  
03 polyalkyl group derived from polyisobutene.  
04
- 05 77. The fuel concentrate according to Claim 60, wherein the  
06 fuel concentrate further contains from about 20 to  
07 about 60 weight percent of a fuel-soluble, nonvolatile  
08 carrier fluid.  
09
- 10 78. The fuel concentrate according to Claim 60, wherein  
11 said poly(oxyalkylene) amine is a hydrocarbyl  
12 poly(oxyalkylene) aminocarbamate.  
13
- 14 79. The fuel concentrate according to Claim 78, wherein the  
15 hydrocarbyl group of said hydrocarbyl poly(oxyalkylene)  
16 aminocarbamate contains from 1 to about 30 carbon  
17 atoms; and wherein the amine moiety of said hydrocarbyl  
18 poly(oxyalkylene) aminocarbamate is derived from a  
19 polyamine having from 2 to 12 amine nitrogen atoms and  
20 from 2 to 40 carbon atoms.
- 21 80. The fuel concentrate according to Claim 79, wherein  
22 said hydrocarbyl group of said hydrocarbyl  
23 poly(oxyalkylene) aminocarbamate is an alkylphenyl  
24 group; and wherein said polyalkylene polyamine is  
25 selected from the group consisting of ethylenediamine,  
26 propylenediamine, diethylenetriamine and  
27 dipropylenetriamine.  
28
- 29 81. The fuel concentrate according to Claim 80, wherein the  
30 alkyl moiety of said alkylphenyl group is  
31 tetrapropenyl.  
32
- 33 82. The fuel concentrate according to Claim 78, wherein  
34 said hydrocarbyl poly(oxyalkylene) aminocarbamate is an



- 01        alkylphenyl poly(oxybutylene) aminocarbamate, wherein  
02        the amine moiety is derived from ethylenediamine or  
03        diethylenetriamine.
- 04        83.    The fuel concentrate according to Claim 60, wherein  
05        said poly(oxyalkylene) amine is a hydrocarbyl  
06        poly(oxyalkylene) monoamine.  
07
- 08        84.    The fuel concentrate according to Claim 83, wherein  
09        said hydrocarbyl poly(oxyalkylene) monoamine is an  
10        alkylphenyl poly(oxyalkylene) monoamine, wherein the  
11        poly(oxyalkylene) moiety contains oxypropylene units or  
12        oxybutylene units or mixtures thereof.  
13
- 14        85.    The fuel concentrate according to Claim 84, wherein the  
15        alkylphenyl group is tetrapropenylphenyl.  
16  
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## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US97/07941**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(6) : C10L 1/18, 1/22

US CL : 44/399, 400; 560/19, 20, 37, 61, 103

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 44/399, 400; 560/19, 20, 37, 61, 103

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4,515,981 A (OTANI ET AL) 07 May 1985 (07-05-85)	1-85
A	US 5,103,039 A (REARDAN ET AL) 07 April 1992 (07-04-92)	1-85
A	US 5,196,565 A (ROSS) 23 May 1993 (23-05-93)	1-85
A	US 5,366,519 A (CHERPECK) 22 November 1994 (22-11-94)	1-85
A,P	US 5,516,342 A (CHERPECK) 14 May 1996 (14-05-96)	1-85
A,P	US 5,540,743 A (CHERPECK) 30 July 1996 (30-07-96)	1-85

☐ Further documents are listed in the continuation of Box C.☐ See patent family annex.

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*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
*O* document referring to an oral disclosure, use, exhibition or other means	
*P* document published prior to the international filing date but later than the priority date claimed	*A* document member of the same patent family

Date of the actual completion of the international search

07 JULY 1997

Date of mailing of the international search report

24 JUL 1997

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